

Non-Empirical Calculation of the π -Electronic States of *Cyclo-Butadiene* Molecule by Valence Bond Method

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Non-empirical calculation of the energy levels of cyclo-butadiene molecule has first been made by Craig¹⁾ from the point of view of molecular orbital method and later a calculation by valence bond method has been performed, using orthogonalized atomic orbitals, by McWeeny^{2~4)}.

In the calculation by Craig a complete basis of antisymmetric molecular orbital configurations has been taken into considerations and, on the other side, in the working of McWeeny all kinds of resonance structures, in which the corresponding bond eigenfunctions are independent linearly, have been taken as a class of canonical structures. The values of energy levels in both of methods, therefore, will arrive at a complete agreement theoretically*. But, afterward, it was pointed out by Shida and Kuri that the numerical value 11.1289 eV. of molecular integral γ_{22} in the paper of Craig should be corrected as 10.5586 eV.⁵⁾ Accordingly, this difference in the numerical values of the molecular integrals may have some effects on the energy levels.

From such a circumstance, in this paper the calculation of the π -electronic energy levels of cyclo-butadiene is carried out by valence bond method, including the complete set of the all π -type resonance structures and considering all kinds of overlap integrals, single exchange integrals, and multiple exchange integrals on the basis of non-orthogonal atomic orbitals. Then relations between the totally

1) D. P. Craig, *Proc. Roy. Soc.*, **A202**, 498 (1950).

2) R. McWeeny, *ibid.*, **A223**, 63 (1954).

3) R. McWeeny, *ibid.*, **A223**, 306 (1954).

4) R. McWeeny, *ibid.*, **A227**, 288 (1955).

* Actually, in the paper of McWeeny it has been reported that the complete agreement of the values of the energy levels with the results by Craig were obtained⁴⁾.

5) S. Shida and Z. Kuri, *J. Chem. Soc. Japan, Pure Chem. Soc.*, (Nippon Kagaku Zasshi), **76**, 322 (1955).

symmetrical state and the non-totally symmetrical state are discussed critically from the point of view of the valence bond method.

Calculation

Cyclo-butadiene was assumed to be a square molecule in which the bond distance between two neighbouring carbon atoms is 1.40Å. Slater 2P-fundtions were used as the atomic orbitals of the four carbon atoms and the screening constant Z_c was taken to have 3.18. π -electron repulsive integrals were taken from the paper of Craig¹⁾ and penetration integrals and core integrals were calculated directly by us according to the method of Parr and Mulliken⁶⁾. The complete set of canonical structures and the energy values corresponding to the structures are shown in Fig. 1, where W_{2p} is the energy of a 2 P _{π} -electron of a carbon atom in its valence state.

Linear combinations of bond eigenfunctions, necessary to present calculations, which are bases for irreducible representations of symmetry group D_{4h} , are inserted in Table I, where ψ_K is the bond eigenfunction for structure K and the representation, including electron spin functions, is given in Table II. In the Table,

TABLE I. RELATIONS BETWEEN BOND EIGENFUNCTIONS AND BASES

${}^1A_{1g}$	$\psi_1 = (1/2)^{1/2}(\psi_A + \psi_B)$
	$\psi_2 = (1/8)^{1/2}(\psi_{C1} + \psi_{C2} + \psi_{D1} + \psi_{D2} + \psi_{E1} + \psi_{E2} + \psi_{F1} + \psi_{F2})$
	$\psi_3 = (1/4)^{1/2}(\psi_{G1} + \psi_{G2} + \psi_{H1} + \psi_{H2})$
	$\psi_4 = (1/2)^{1/2}(\psi_{I1} + \psi_{I2})$
	$\psi_5 = (1/4)^{1/2}(\psi_{J1} + \psi_{J2} + \psi_{K1} + \psi_{K2})$
${}^1B_{1g}$	$\psi_2 = (1/8)^{1/2}(\psi_{C1} - \psi_{C2} + \psi_{D1} - \psi_{D2} + \psi_{E1} - \psi_{E2} + \psi_{F1} - \psi_{F2})$
	$\psi_3 = (1/4)^{1/2}(\psi_{G1} - \psi_{G2} + \psi_{H1} - \psi_{H2})$
	$\psi_4 = (1/2)^{1/2}(\psi_{I1} - \psi_{I2})$
${}^1B_{2g}$	$\psi_1 = (1/2)^{1/2}(\psi_A - \psi_B)$
	$\psi_2 = (1/8)^{1/2}(\psi_{C1} + \psi_{C2} + \psi_{D1} + \psi_{D2} - \psi_{E1} - \psi_{E2} - \psi_{F1} - \psi_{F2})$
	$\psi_5 = (1/4)^{1/2}(\psi_{J1} + \psi_{J2} - \psi_{K1} - \psi_{K2})$

6) R.G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

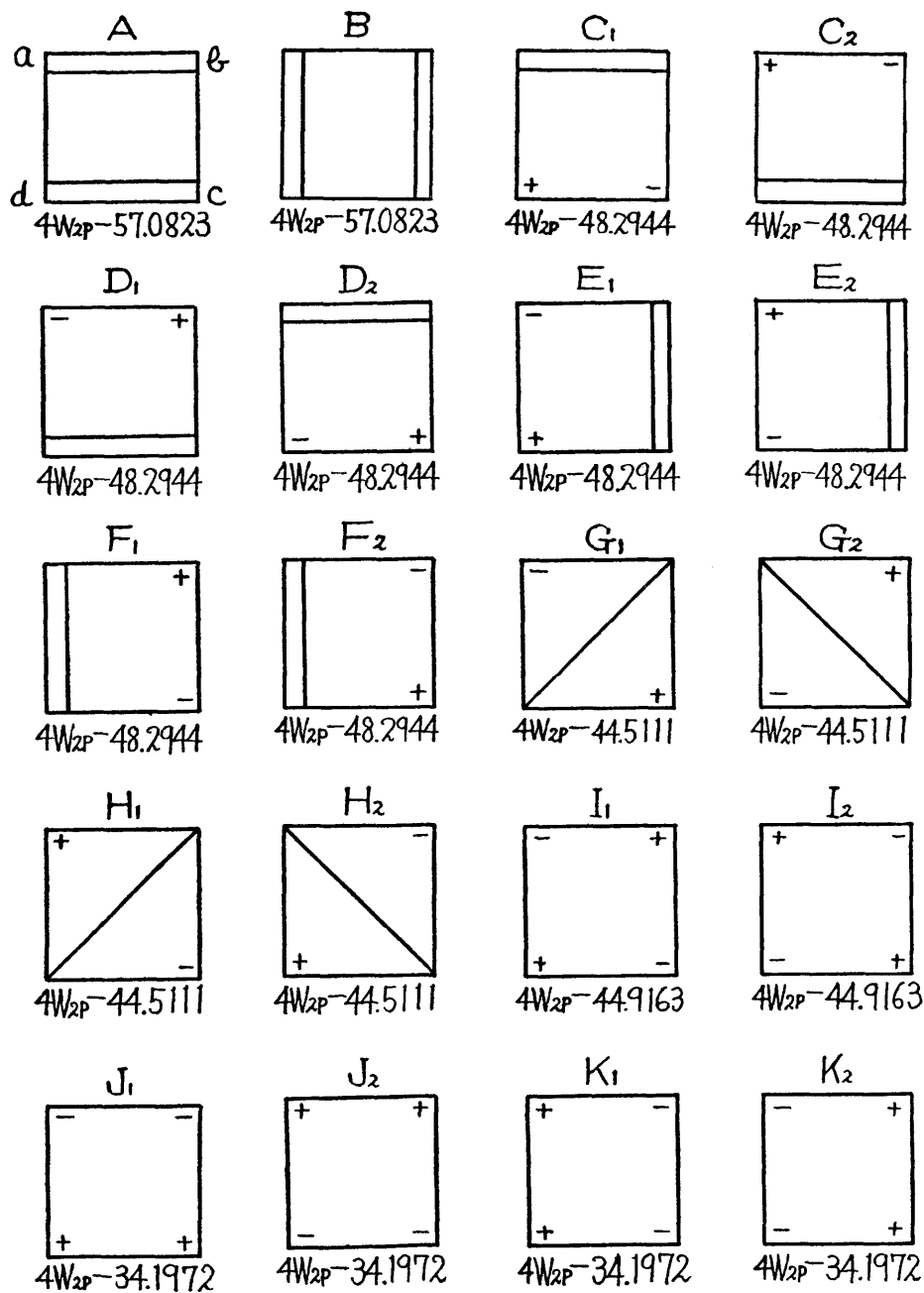


Fig. 1. Canonical structures of cyclo-butadiene and the numerical values of the energies for the structures. (Values are in electron volts.)

TABLE II. BOND EIGENFUNCTIONS

$$\begin{aligned}
\psi_A &= (1/4)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)b(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \\
&\quad c(3)d(4)\{\alpha(3)\beta(4) - \beta(3)\alpha(4)\}] \\
\psi_B &= (1/4)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)d(4)\{\alpha(1)\beta(4) - \beta(1)\alpha(4)\} \\
&\quad b(2)c(3)\{\alpha(2)\beta(3) - \beta(2)\alpha(3)\}] \\
\psi_{c1} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)b(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \\
&\quad c(3)c(4)\{\alpha(3)\beta(4)\}] \\
\psi_{c2} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[b(1)b(2)\{\alpha(1)\beta(2)\}c(3)d(4) \\
&\quad \{\alpha(3)\beta(4) - \beta(3)\alpha(4)\}] \\
\psi_{d1} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)a(2)\{\alpha(1)\beta(2)\}c(3)d(4) \\
&\quad \{\alpha(3)\beta(4) - \beta(3)\alpha(4)\}] \\
\psi_{d^2} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)b(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \\
&\quad d(3)d(4)\{\alpha(3)\beta(4)\}] \\
\psi_{e1} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)a(2)\{\alpha(1)\beta(2)\}b(3)c(4) \\
&\quad \{\alpha(3)\beta(4) - \beta(3)\alpha(4)\}] \\
\psi_{e2} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[b(1)c(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \\
&\quad d(3)d(4)\{\alpha(3)\beta(4)\}] \\
\psi_{f1} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)d(4)\{\alpha(1)\beta(4) - \beta(1)\alpha(4)\} \\
&\quad c(2)c(3)\{\alpha(2)\beta(3)\}] \\
\psi_{f2} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)d(4)\{\alpha(1)\beta(1) - \beta(1)\alpha(4)\} \\
&\quad b(2)b(3)\{\alpha(2)\beta(3)\}] \\
\psi_{g1} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)a(2)\{\alpha(1)\beta(2)\}b(3)d(4) \\
&\quad \{\alpha(3)\beta(4) - \beta(3)\alpha(4)\}] \\
\psi_{g2} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)c(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \\
&\quad d(3)d(4)\{\alpha(3)\beta(4)\}] \\
\psi_{H1} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[b(1)d(4)\{\alpha(1)\beta(4) - \beta(1)\alpha(4)\} \\
&\quad c(2)c(3)\{\alpha(2)\beta(3)\}] \\
\psi_{H2} &= (1/2)^{1/2} (1/4!)^{1/2} \sum_P (-1)^P P[a(1)c(4)\{\alpha(1)\beta(4) - \beta(1)\alpha(4)\} \\
&\quad b(2)b(3)\{\alpha(2)\beta(3)\}] \\
\psi_{I1} &= (1/4!)^{1/2} \sum_P (-1)^P P[a(1)a(2)\{\alpha(1)\beta(2)\}c(3)c(4)\{\alpha(3)\beta(4)\}] \\
\psi_{I2} &= (1/4!)^{1/2} \sum_P (-1)^P P[b(1)b(2)\{\alpha(1)\beta(2)\}d(3)d(4)\{\alpha(3)\beta(4)\}]
\end{aligned}$$

$$\begin{aligned}
\psi_{r_1} &= (1/4!)^{1/2} \sum_P (-1)^P P[a(1)a(2)\{\alpha(1)\beta(2)\}b(3)b(4)\{\alpha(3)\beta(4)\}] \\
\psi_{r_2} &= (1/4!)^{1/2} \sum_P (-1)^P P[c(1)c(2)\{\alpha(1)\beta(2)\}d(3)d(4)\{\alpha(3)\beta(4)\}] \\
\psi_{r_{k1}} &= (1/4!)^{1/2} \sum_P (-1)^P P[b(1)b(2)\{\alpha(1)\beta(2)\}c(3)c(4)\{\alpha(3)\beta(4)\}] \\
\psi_{r_{k2}} &= (1/4!)^{1/2} \sum_P (-1)^P P[a(1)a(2)\{\alpha(1)\beta(2)\}d(3)d(4)\{\alpha(3)\beta(4)\}]
\end{aligned}$$

P means the permutation of electrons, $k(i)$ is the atomic orbital of electron i on atom k , and $\alpha(i)$, $\beta(i)$ are the two spin functions.

In our approximation the Hamiltonian operator \mathbf{H} is expressed in the form

$$\mathbf{H} = \sum_i \mathbf{H}_{core}(i) + (1/2) \sum_{i,j} (\mathbf{e}^2/r_{ij}),$$

where

$$\mathbf{H}_{core}(i) = \mathbf{T}(i) + \mathbf{U}_{core}(i),$$

where $\mathbf{T}(i)$ is the kinetic energy operator for electron i and $\mathbf{U}_{core}(i)$ is the potential energy operator for the electron in the field of the core.

Numerical values of two kinds of integrals, appear in the cases of the calculations of the interactions of bond eigenfunctions, are listed in Table III, where $ij : kl$ is the bond eigenfunction for the structure in which there are double bonds between atoms i and j , atoms k and l , respectively.

And then the values of matrix elements, required to solve secular determinants, are shown in Table IV.

TABLE III. INTERACTIONS BETWEEN BOND EIGENFUNCTIONS

$\psi_K - \psi_L$	$H_{KL} = \int \psi_K \mathbf{H} \psi_L d\tau$	$S_{KL} = \int \psi_K \psi_L d\tau$
(ab : cd - ab : cd)	-59.2749	+1.03841
(ab : cd - ad : bc)	+35.1844	-0.599996
(ab : cd - ab : cc)	-20.0772	+0.327427
(ab : cd - aa : bc)	+10.0822	-0.163713
(ab : cd - aa : bd)	+1.26959	-0.0158983
(ab : cd - aa : cc)	-3.63533	+0.0545180
(ab : cd - aa : bb)	+3.59489	-0.0551765
(ab : cd - bb : cc)	-7.02051	+0.108378
(ab : cc - ab : cc)	-47.3559	+0.980568
(ab : cc - bb : cd)	-3.53605	+0.0545180
(ab : cc - aa : cd)	-7.49687	+0.111704

$(ab : cc - ab : dd)$	-3.73954	+0.0545180
$(ab : cc - aa : bc)$	+1.28106	-0.0290749
$(ab : cc - bc : dd)$	+3.65112	-0.0545180
$(ab : cc - ad : cc)$	-5.13877	+0.0799615
$(ab : cc - aa : bd)$	+0.436991	-0.0 ² 747450
$(ab : cc - ac : dd)$	+1.50692	-0.0194569
$(ab : cc - bd : cc)$	-12.3605	+0.224051
$(ab : cc - ac : bb)$	+11.6793	-0.212069
$(ab : cc - aa : cc)$	-18.0573	+0.327427
$(ab : cc - bb : dd)$	+0.0 ² 726361	0
$(ab : cc - aa : bb)$	+0.761674	-0.0 ² 847284
$(ab : cc - cc : dd)$	-0.635043	+0.0 ² 847284
$(ab : cc - bb : cc)$	-15.4578	+0.308383
$(ab : cc - aa : dd)$	-1.39639	+0.0190434
$(aa : bd - aa : bd)$	-38.8515	+0.872849
$(aa : bd - ac : dd)$	+3.42805	-0.0532015
$(aa : bd - bd : cc)$	-0.314009	+0.0 ² 398436
$(aa : bd - aa : cc)$	-4.84234	+0.0771001
$(aa : bd - bb : dd)$	+4.95689	-0.0771001
$(aa : bd - aa : bb)$	-2.28416	+0.0338894
$(aa : bd - cc : dd)$	+0.203008	-0.0 ² 209275
$(aa : cc - aa : cc)$	-44.1633	+0.983235
$(aa : cc - bb : dd)$	+0.0 ² 483771	0
$(aa : cc - aa : bb)$	-3.27196	+0.0545182
$(aa : bb - aa : bb)$	-29.8265	+0.872190
$(aa : bb - cc : dd)$	-0.267553	+0.0 ² 332596
$(aa : bb - bb : cc)$	-0.0230413	+0.0 ³ 658396

TABLE IV MATRIX ELEMENTS

$$H_{ij} = \int \psi_i \mathbf{H} \psi_j d\tau, \quad S_{ij} = \int \psi_i \psi_j d\tau$$

${}^1A_{1g}$			
$H_{11} = -24.0906$	$S_{11} = +0.438416$	$H_{25} = -23.6563$	$S_{25} = +0.463052$
$H_{12} = -19.9399$	$S_{12} = +0.327427$	$H_{33} = -32.3094$	$S_{33} = +0.770430$
$H_{13} = +3.59093$	$S_{13} = -0.0449673$	$H_{34} = +0.162000$	$S_{34} = 0$
$H_{14} = -7.27066$	$S_{14} = +0.109036$	$H_{35} = -4.16231$	$S_{35} = +0.0635933$
$H_{15} = -4.84457$	$S_{15} = +0.0752381$	$H_{44} = -44.1584$	$S_{44} = +0.983235$
$H_{22} = -58.6839$	$S_{22} = +1.14316$	$H_{45} = -9.25450$	$S_{45} = +0.154201$
$H_{23} = +1.78572$	$S_{23} = -0.0211411$	$H_{55} = -30.1401$	$S_{55} = +0.876833$
$H_{24} = -36.1002$	$S_{24} = +0.654854$		

${}^1B_{1g}$			
$H_{22} = -58.7372$	$S_{22} = +1.14316$	$H_{33} = -38.5375$	$S_{33} = +0.868864$
$H_{23} = -35.5104$	$S_{23} = +0.633713$	$H_{34} = -13.8582$	$S_{34} = +0.218073$
$H_{24} = -36.1292$	$S_{24} = +0.654854$	$H_{44} = -44.1681$	$S_{44} = 0.983235$

${}^1B_{2g}$			
$H_{11} = -94.4593$	$S_{11} = +1.63841$	$H_{22} = -65.5729$	$S_{22} = +1.25946$
$H_{12} = -60.3188$	$S_{12} = +0.982281$	$H_{25} = +24.0145$	$S_{25} = -0.463052$
$H_{15} = +15.0124$	$S_{15} = -0.231301$	$H_{55} = -30.0479$	$S_{55} = +0.874199$

Numerical values of orbital energies for the molecule, evaluated using these values, and the corresponding wave functions, found by the application of normalization condition, are collected in Table V.

TABLE V. WAVE FUNCTIONS FOR THE MOLECULE AND THE CORRESPONDING ORBITAL ENERGIES

$$\Phi_1({}^1B_{2g}) = 0.80023\phi_1 + 0.26085\phi_2 - 0.01111\phi_3$$

$$E_1 = 4W_{2p} - 58.3517 \text{ eV.}$$

$$\Phi_2({}^1A_{1g}) = 0.75393\phi_1 + 0.32697\phi_2 - 0.11784\phi_3 + 0.09264\phi_4 - 0.00386\phi_5$$

$$E_2 = 4W_{2p} - 56.3627 \text{ eV.}$$

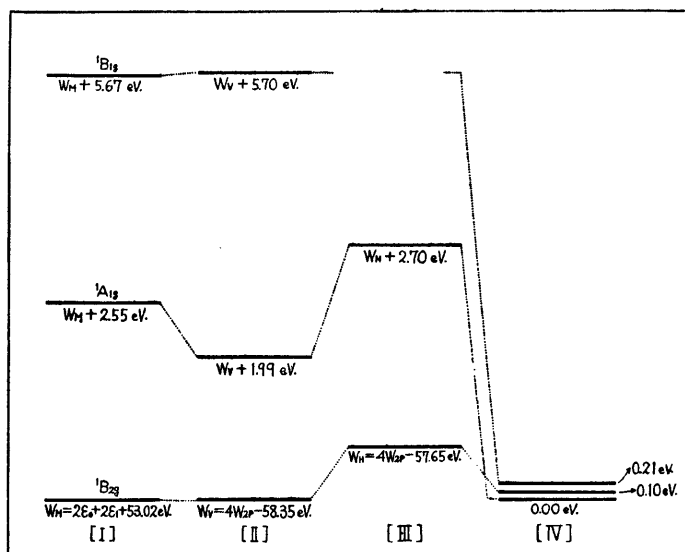
$$\Phi_3({}^1B_{1g}) = 0.68396\phi_2 + 0.24527\phi_3 + 0.21925\phi_4$$

$$E_3 = 4W_{2p} - 52.6519 \text{ eV.}$$

ϕ_i is the normalized representation of base ψ_i .

Discussion

Energy levels of cyclo-butadiene molecule, calculated in the foregoing paragraph, are shown in Fig. 2 diagrammatically together with the results of Craig by the method of ASMOCI and of Moffitt and Scanlan⁷⁾ by the method of atoms in molecule.



I. ASMO. CI.¹⁾ II. HLSP III. Heitler-London IV. AIM.⁷⁾

Fig. 2. Comparison of energy levels.

It is impossible to count directly from the Figure how much discrepancy rose for the value of the orbital energy in the ground state of the molecule by the numerical error of molecular integral γ_{22} , since the bases of the energy zeros in the calculations between (I) and (II) are different. It is noticed that the $1A_{1g}$ level, evaluated by us, is lower by 0.56 eV. relatively than the result of Craig and this difference is nearly the same as that in the value of the molecular integral.

Now, in such a molecule, in which the bond eigenfunctions for the Kekule structure and the Dewar structure belong to an identical base, as in cyclobutadiene molecule**, negative resonance effects appear in the interactions of

7) W. Moffitt and J. Scanlan, *Proc. Roy. Soc.*, **A202**, 498 (1950).

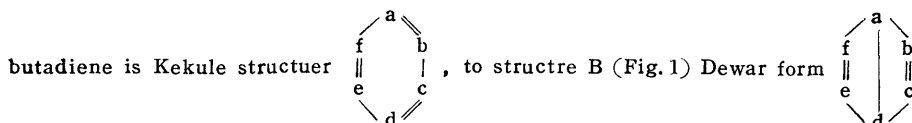
these two kinds of the bond eigenfunctions in the totally symmetrical state and, therefore, the energy level for the lowest state is held higher than the value of the energy for a Kekule structure.

Considering that the bond eigenfunction for an ionic structure is induced from the bond eigenfunction for a specific covalent structure⁸⁾, it may be supposed that the phenomena of showing negative resonance effects, mentioned above, will also appear in the cases of interactions among ionic structures ***. In fact, it is recognized in Table VI that in the bases in which the value of subscript i is

TABLE VI. RELATIONS BETWEEN BASES AND THEIR ENERGY VALUES

	ψ_1	ψ_2	ψ_3	ψ_4
¹ B _{2g} -state	4W _{2p} -57.6531	4W _{2p} -52.0644	—————	—————
¹ A _{1g} -state	4W _{2p} -54.9491	4W _{2p} -51.3349	4W _{2p} -41.9368	4W _{2p} -44.9113
¹ B _{1g} -state	—————	4W _{2p} -51.3815	4W _{2p} -44.3538	4W _{2p} -44.9212
<hr/>				
	ψ_5			
¹ B _{2g} -state	4W _{2p} -34.3720	Values are in electron volts.		
¹ A _{1g} -state	4W _{2p} -34.3738			
¹ B _{1g} -state	—————			

** Though the structure of benzene corresponding to structure A (Fig. 1) in cyclo-



corresponds, since there are double bonds between a and d, b and c, respectively. Practically, the signs of bond eigenfunctions are able to be decided automatically in this point of view.

8) D. P. Craig, *Proc. Roy. Soc.*, **A200**, 390 (1950).

*** In the cases of complicated ionic structures positive resonance effects will appear partially by interactions, since there may be cases that an identical ionic structure is induced from two or the more kinds of covalent structures.

small, in other words, and which are comparatively important to the resonance effects in the ground state, the values of the corresponding energies are lower in the non-totally symmetrical ${}^1B_{2g}$ states than in the totally symmetrical ${}^1A_{1g}$ states.

Accordingly, it seems that the interactions among the bases give very important effects on lowering the totally symmetrical level, not among the bond eigenfunctions, of which a base consists.

Summary

π -electronic energy levels of cyclo-butadiene molecule have been calculated non-empirically by the standard valence bond method, including all kinds of overlap, single exchange, and multiple exchange integrals. The resultant value of the transition energy between the ground ${}^1B_{2g}$ -state and the first excited ${}^1A_{1g}$ -state is 1.99 eV. (Craig's result is 2.55 eV.) The calculation has been also attempted by Heitler-London method. Comparisons of these values with the results by molecular orbital calculations have been made.

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